Hexavalent Chromium Control in Hard Chrome Electroplating Baths Using a Wetting Agent Fume Suppressant (WA/FS)

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Project Financial Support

- DOD Environmental Security & Technology Certification Program
- Focus is on environmental issues
- But … can slip in OSH/IH

- http://www.estcp.org/

- Project 20003 - FY00/01/02

What is WA/FS?

- Liquid surfactant mixed into to hard chrome solutions
- Reduces solution surface tension
- Inhibits bubble formation
  - smaller, more fragile bubbles
  - less mist at bursting
  - lower occupational exposures
  - lower air emissions

WAFS in Action

Drop-in Solution -

Simply add appropriate amount to an existing tank

Project Objectives

Demonstrate the effects of adding WAFS to DOD hard chrome tanks

- Target surface tension of 25 +/- 2 dynes/cm
- Determine hexavalent chrome indoor and outdoor air emissions reduction at two locations
  - Artisan exposure goal - below 0.0005 mg/m^3
  - Stack air emission goal - below 0.015 mg/dscm
- Evaluate effect of WA/FS on material quality at three locations

US EPA Standards for Chromium Plating and Anodizing Baths

Type of Bath	Emission Limitations	
	Small Facility (<60 million amp-hrs/yr)	Large Facility
Hard Chromium Plating Baths		
All existing baths	0.03 milligrams/dry standard cubic meter (mg/dscm) (1.3×10^{-5} grains/dry standard cubic foot [gr/dscf])	0.015 mg/dscm (6.6×10^{-6} gr/dscf)
All new baths	0.015 mg/dscm (6.6×10^{-6} gr/dscf)	0.015 mg/dscm (6.6×10^{-6} gr/dscf)
Decorative Chromium Plating Baths Using Chromic Acid		
All new and existing baths	**0.01 mg/dscm (4.4×10^{-6} gr/dscf) or Surface Tension <45 dynes/centimeter**	
Chromium Anodizing Baths		
All new and existing baths	**0.01 mg/dscm (4.4×10^{-6} gr/dscf) or Surface Tension - <45 dynes/centimeter**	

Demonstration Sites

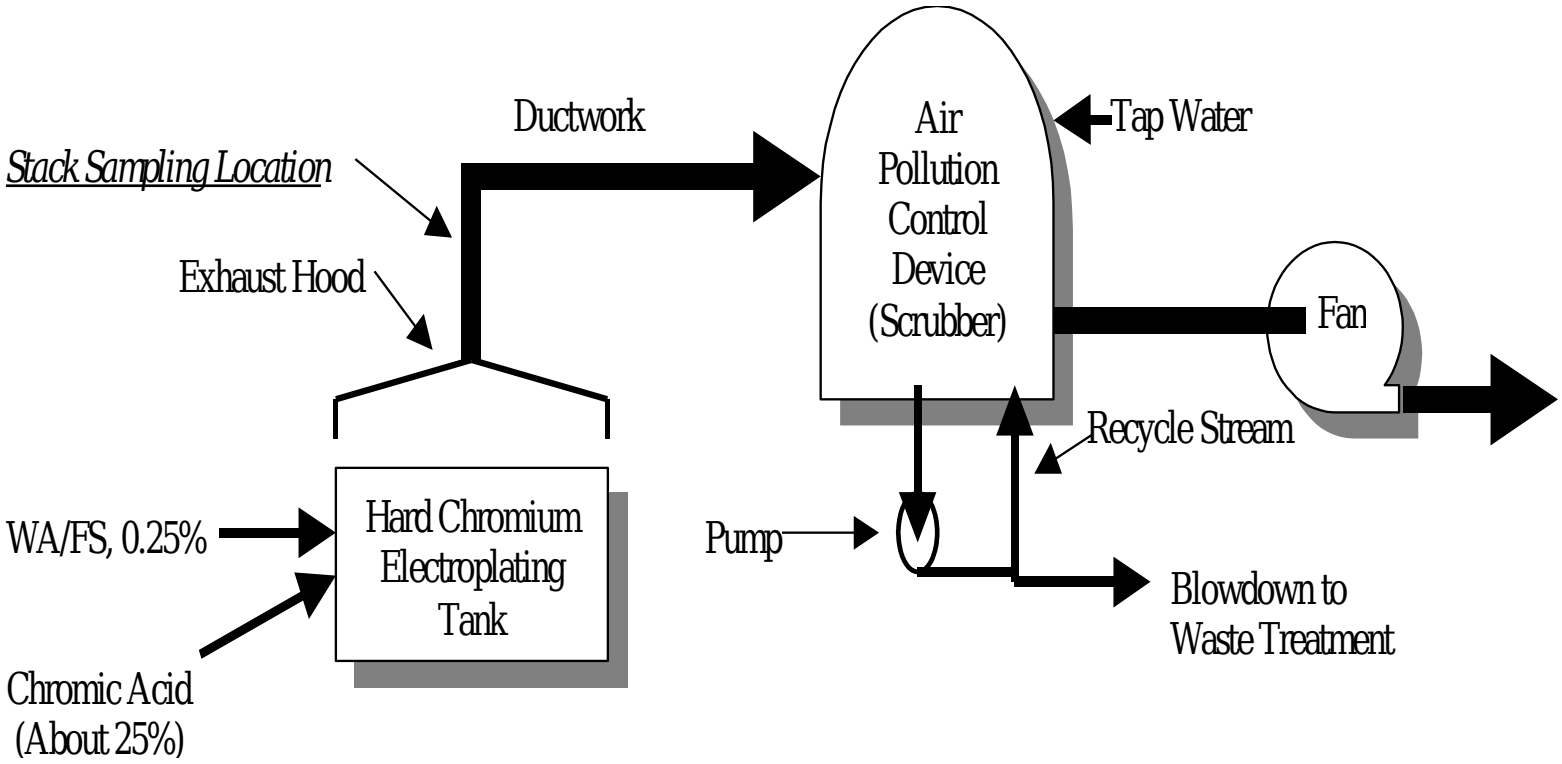
Air Emissions (OSH&E)

- NADEP Cherry Point
- ALC Oklahoma City

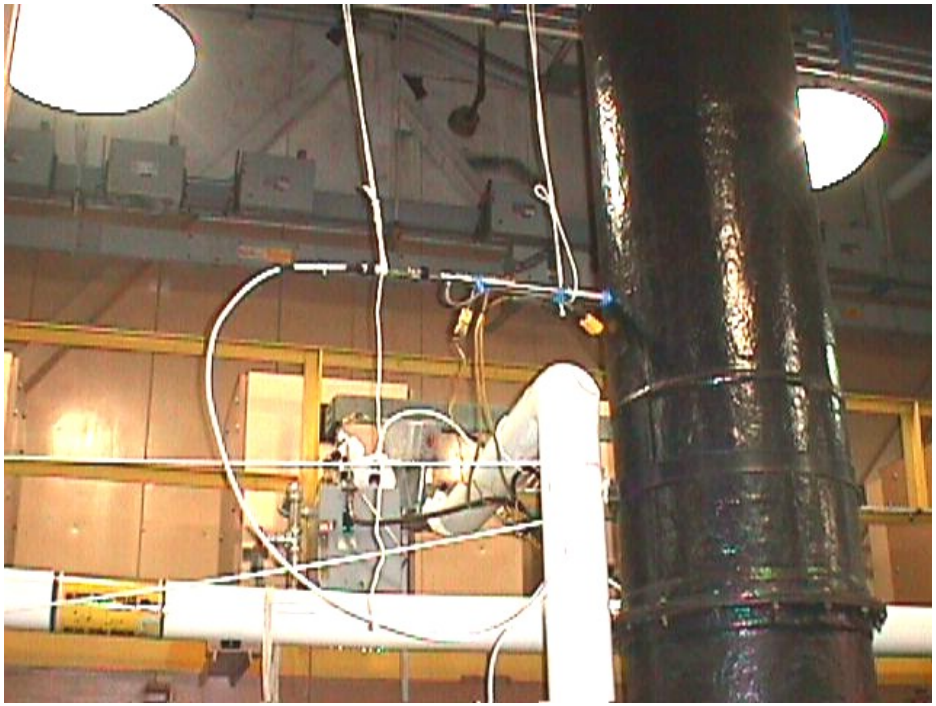
Material Quality

- NADEP Cherry Point
- ALC Oklahoma City
- NADEP North Island

Process Schematic and Description



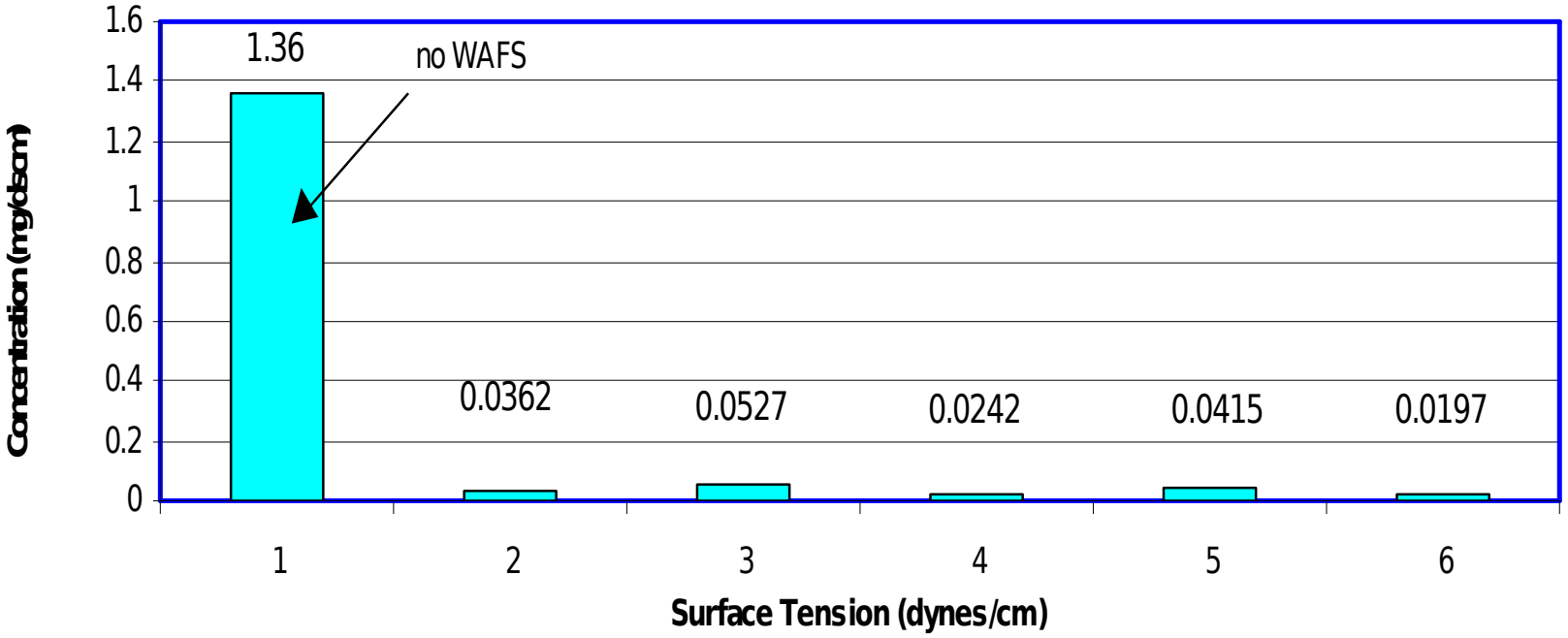
EPA Test Method 306



Total Chromium Concentrations in Stack Emissions

NADEP Cherry Point

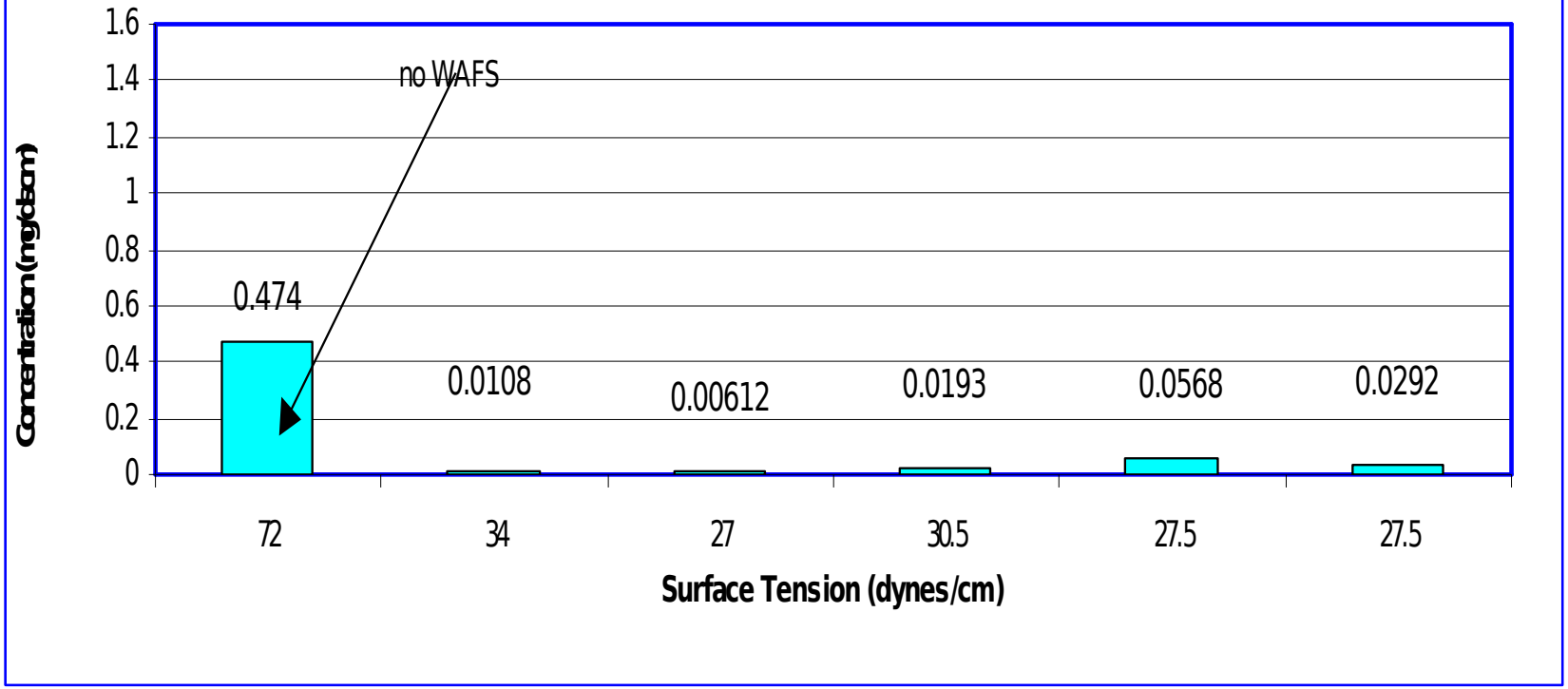
40-fold reduction in Total Cr
97.5 %reduction in Total Cr



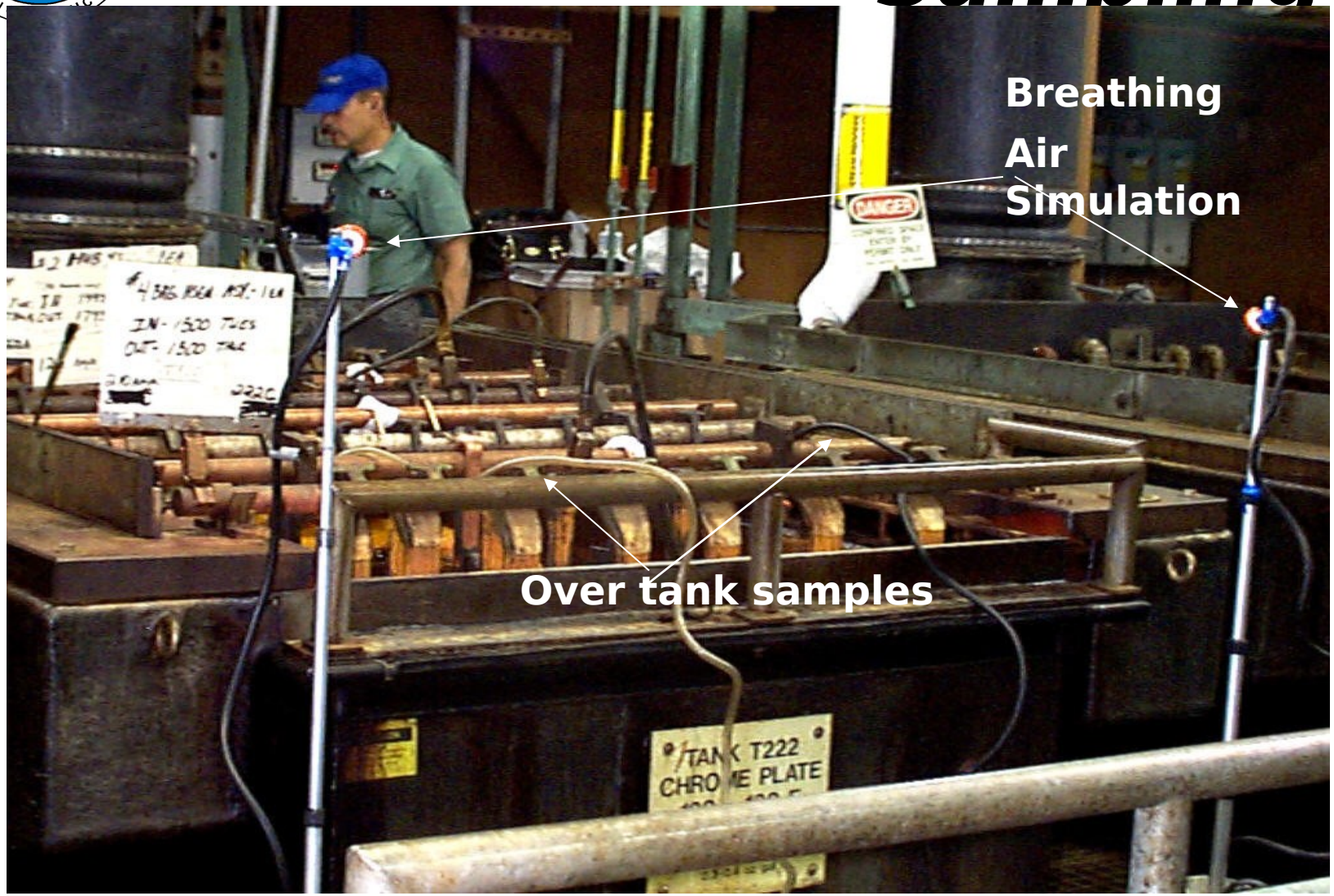
Total Chromium Concentrations in Stack Emissions

ALC - Oklahoma City

19-fold reduction in Total Cr
94.8% reduction in Total Cr



IH Engineering Sampling



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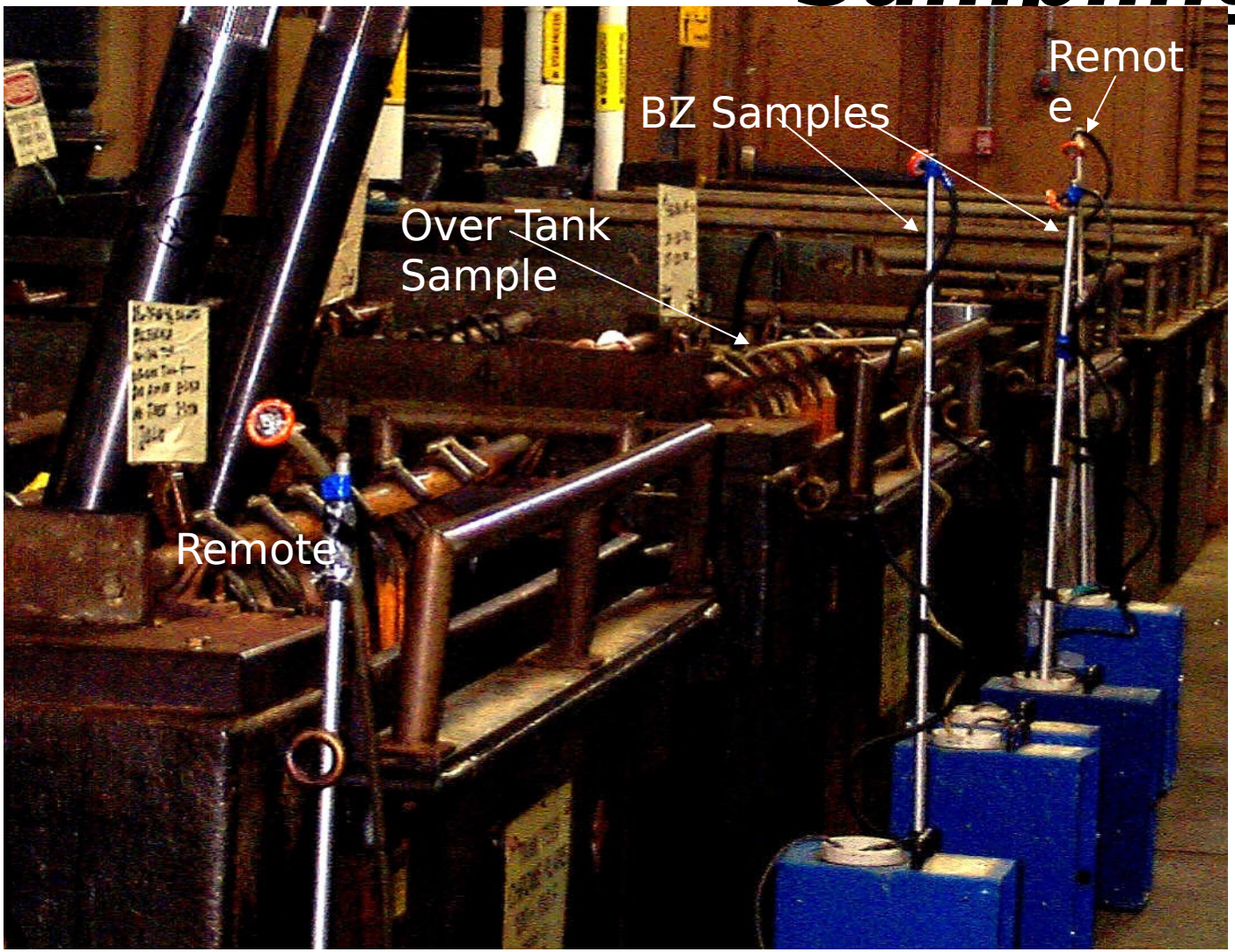


Industrial Hygiene Engineering Samples

Average concentrations (micrograms/cubic meter)							
NADEP Cherry Point				ALC-OKC (Tinker)			
	Remote Breathing Zone	Near Tank Breathing Zone	In Tank		Remote Breathing Zone	***Near Tank Breathing Zone***	In Tank
w/o WAFS	**0.043**	**0.076**	**1.842**	w/o WAFS	**0.083**	***0.018***	**1.561**
with WAFS	**0.026**	**0.052**	**0.070**	with WAFS	**0.026**	***0.031***	**0.054**

Influence of Exhaust Parameters on Emissions Concentration

	Bath Surface Area (ft^2)	Average Exhaust Volumetric Flow (dscfm)	Free-board (inches)	Exhaust Intake Area (ft^2)	Volume per Unit Surface Area (cfm/ft^2)	Exhaust Intake Velocity (fpm)	Hexavalent Chromium Concent. in Bath (%)	Exhaust Configuration
Cherry Point	21.5	6,350	8	3.22	295	1,970	15.1	"Pull"-only system. One lip vent on back (long side), with back wall.
Tinker	26.8	7,160	7-1/2	2.65	267	2,700	12.6	"Pull"-only system. One lip vent on each long side. Stand-alone bath.

Technical Performance

NAVAIR tested 560 samples

QQ-C-320B **Material Quality Tests**

- Hydrogen Embrittlement
  - **200 hr Sustained Load**
  - **Rising Step**
- Coating Adhesion
- Thickness
- Hardness
- Pitting
- Porosity

10 coupons or round bar samples per test
Each test repeated eight times

Technical Performance

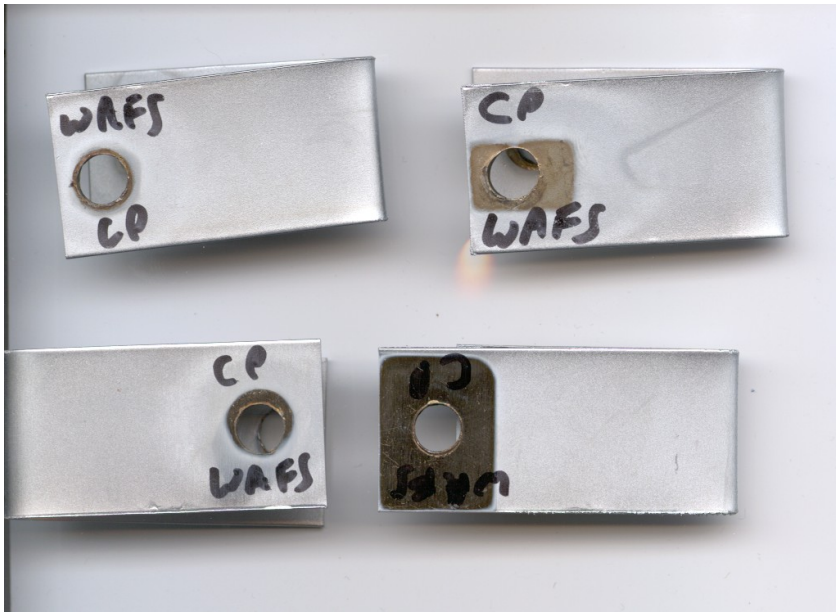
Fatigue Testing - This is the make or break materials test

- Plated with and without WAFS at CP in Jan-March
- Fatigue testing to begin at Pax when plated samples received
- Testing expected to take 3 months

Test Results

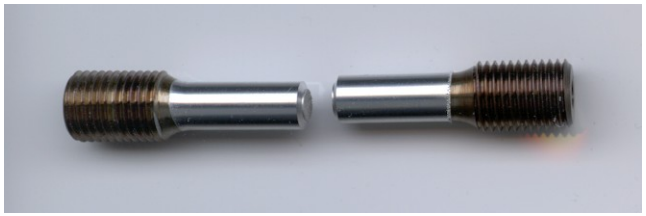
Coating Adhesion

- **Mixed results for 180 degree mandrel bend test**
  - *Samples pass at one facility fail at the other two*
  - *Appears to be related to site specific sample surface prep, not WAFS.*
- Repeat test 3 mil samples.



Test Results

- Hardness Testing
  - initial surface Rockwell microhardness tests completed at Pax: substrate affected measurements
  - NADEP CP completing Vickers (HV100) test on edge of coating to eliminate substrate effect
- Pitting & Porosity test completed



Notched round bar
after 24-hr tensile test

Test Results

Hydrogen Embrittlement

No effect was due to WAFS

- Standard 200 hour sustained load: All samples meet ASTM spec/ performed by Dirats Lab
- 24 hour rising step load - no difference in performance between control and WAFS NAVAIR/ Inorganic Coatings

Annual Savings Using WA/FS

(Dollars per hard chromium plating bath)*

	Existing Hard Chromium Line		New Hard Chromium Line
	WA/FS plus scrubber	WA/FS with scrubber disabled	
Startup Costs	800	4,390	(45,200)
Annualized Startup Costs/Savings**	95	520	(5,350)
Annual O&M Costs/Savings	(400)	(8,100)	(8,100)
Total Annual Cost/Savings	(300)	(7,600)	(13,450)
Payback Period (years)	2.7	0.6	N/A

* Savings are in parentheses ( ).

**Annualized costs/savings are calculated based on 10 years equipment life for capital equipment, and a Real Discount Rate of 3.2% per year.

Perfluorooctyl Sulfonates (PFOS) Analyses

PFOS Compound	Stack Test Liquid Sample (µg/l)	Equivalent Stack Emissions to Scrubber (mg/dscm)	Scrubber Effluent Holding Tank (µg/l)	IWTP Influent (µg/l)	Blank (µg/l)
Perfluorooctane Sulfonate	39	0.0049	11	<10	<10
2-(N-ethylperfluorooctane sulfonamido) ethyl alcohol (PFOSA)	10*	0.0013*	<10	<10	11

- Assumed to be 0.0 µg/l since the PFOSA detected in the blank exceeded the PFOSA detected in the actual sample. Similarly, the equivalent stack emission is assumed to be 0.0000 mg/dscm.

New SNUR issued March 2002

Disadvantages

- Plating solutions made with ***hard water*** don’t approach regulatory mandated Surface Tension

- ***Environmental Fate*** is a potential concern
  - Difficult and costly to remove from tank

Advantages

- Environmental Air Emissions - achieved ~ average ***30-fold reduction*** in hexavalent and total chromium
- ***Low artisan exposures*** - ~ anticipated OSH PEL
- Material quality performance - ***equal to or better*** than conventional Cr $^{+6}$ baths Permanently ***stable*** fume suppressant
- An easy ***drop in*** solution to implement
- Foam blanket primarily at the anode and cathode
- Very ***inexpensive***

Questions?